Measurement of Trace Explosive Residues in a Surrogate Operational Environment: Implications for Tactical Use of Chemical Sensing in C-IED Operations*

Roderick R. Kunz, Kerin Clow, Dennis Hardy
Lincoln Laboratory, Massachusetts Institute of Technology, Lexington, MA 02420

Augustus Way Fountain III, Stanley A. Ostazeski, and Jonathan Oyler
Chemical-Biological Detection, Edgewood Chemical Biological Center,
Aberdeen Proving Ground, MD 21010-5424

ABSTRACT

A campaign to measure the amount of trace explosive residues in an operational military environment was conducted on May 27-31, 2007, at the National Training Center at Fort Irwin, CA. The objectives to this campaign were to develop the methods needed to collect and analyze samples from tactical military settings, to use the data obtained to determine what the trace-explosive signatures suggest about the potential capabilities of chemical-based means to detect IEDs and IED-related threats under tactical conditions, and finally, to present a framework whereby a sound understanding of the signature science can be used to guide development of new sensing technologies and sensor concepts of operation. Through our use of combined background and threat signature data, we have performed statistical analyses to estimate upper limits of notional sensor performance that is limited only by the spatial correlation of the signature chemicals to the threats of interest. Here, the threats were surrogate IEDs used in situational training exercises at the National Training Center. Even for this best case detection scenario, we estimate that tactical use of explosives detection to locate IEDs and/or IED-related threats will likely not support high detection probabilities (i.e., <50% PD at best) or low false alarm rates (i.e., >5% PFA likely). This is because, although explosive residues <u>are</u> spatially correlated with IED-related threats, the correlation is weak. Specifically, it was determined that only 27% of all IED-related threats exhibited trace explosive residues exceeding 1 µg on/in their immediate vicinity, whereas for general background measurements this fraction was <1%. However, 6% of background measurements taken from live-fire areas recorded contamination levels in excess of 1 µg. A greater understanding of explosives residue fate and transport is needed to further refine these estimates.

1. INTRODUCTION

The well-recognized threat from improvised explosive devices (IEDs) has mobilized an aggressive counter-strategy involving new training methods, operational doctrine, and technological solutions. Amongst the candidate technologies considered for counter-IED operations, stand-off trace chemical detection is consistently perceived as worthy of further development because the chemistry of the explosive charge is seen as the only common thread linking all IED designs. This perception has led to generous support of trace detection methods from the research and development community. As important and worthy as these endeavors are, the ultimate effectiveness of such detection systems under tactical conditions may not be hardware limited, but rather limited by the availability, abundance, persistence, and/or spatial distribution of the trace chemical residues they've been designed to detect. In short, uncertainties regarding the fate, transport, and overall phenomenological behavior of the IED's chemical signatures may be more limiting to the performance of such systems than the hardware itself, and thus efforts must be made to understand this "signature science" in parallel to the technology development efforts.

In this effort, personnel from the Massachusetts Institute of Technology's Lincoln Laboratory (MIT-LL) and the U.S. Army's Edgewood Chemical-Biological Forensic Analytical Center (EC/B-FAC) teamed in an effort directed by the U.S. Army's Edgewood Chemical and Biological Center (ECBC) and supported by Joint Improvised Explosive Device Defeat Organization (JIEDDO). The focus of this joint effort was to perform comprehensive, detailed trace explosive measurements in settings serving as surrogates for realistic tactical settings, and to perform analysis of the results to generate statistical bases for performance expectations of emerging trace detection methods.

For these purposes, two laboratory analytical techniques were used. First, method AM-183 based on gas chromatography mass spectrometry (GC-MS) was developed at the Edgewood Chemical and Biological Center and it was used in combination with a dual gas-chromatography electron-capture detection (GC-ECD)[2] method based on

Report Documentation Page	Form Approved *OMB No. 0704-0188*

Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.

1. REPORT DATE **01 DEC 2008**	2. REPORT TYPE **N/A**	3. DATES COVERED **-**	
4. TITLE AND SUBTITLE **Measurement of Trace Explosive Residues in a Surrogate Operational Environment: Implications for Tactical Use of Chemical Sensing in C-IED Operations**		5a. CONTRACT NUMBER	
		5b. GRANT NUMBER	
		5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)		5d. PROJECT NUMBER	
		5e. TASK NUMBER	
		5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **Lincoln Laboratory, Massachusetts Institute of Technology, Lexington, MA 02420**		8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)		10. SPONSOR/MONITOR'S ACRONYM(S)	
		11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT **Approved for public release, distribution unlimited**			
13. SUPPLEMENTARY NOTES **See also ADM002187. Proceedings of the Army Science Conference (26th) Held in Orlando, Florida on 1-4 December 2008, The original document contains color images.**			
14. ABSTRACT			
15. SUBJECT TERMS			

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**	**UU**	**16**	

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std Z39-18

Environmental Protection Agency Analytical Method 8095 and developed at MIT-Lincoln Laboratory. The GC-MS method allowed for identification of a PETN thermal degradant not previously calibrated for by electron capture detection and provided detailed structural and conformational information thereby providing a superior means to identify energetic compounds, and was thus less prone to performance limitations stemming from chemically contaminated environmental samples. However, the GC-MS method did not match the superior sensitivity of the (GC-ECD)[2]. Thus, the two methods used in combination provided an unprecedented level of rigor in performing these studies.

Using the combined results from both methods, 817 sample locations measured during this campaign at Fort Irwin were classified by threat state, operational background, and sample type (see Table 1). The trace explosive results from this campaign indicate that environmental explosive residues are spatially correlated with IED-related threats, although the correlation is weak. For example, it was determined that 27% of all IED-related threats exhibited trace explosive residues exceeding 1 μg on/in their immediate vicinity, whereas for general background measurements this fraction was <1%. However, 6% of background measurements taken from live-fire areas recorded contamination levels in excess of 1 μg. From these results, and additional analysis reported in Section 4 of this report, it can be concluded that tactical use of explosives detection to locate IEDs and/or IED-related threats will likely not support high detection probabilities (i.e., <50% PD at best) or low false alarm rates (i.e., >5% PFA likely). However, the data in this report also suggests new strategies may be possible that might provide capabilities not afforded by currently pursued detection strategies. For example, it was determined that RDX residues on surfaces, detected at low threshold (<300 ng) might afford modest detection probabilities of ~20% but maintain false alarm rates <1%. Likewise, it was determined that 2,4-dinitrotoluene residue in soils caused by munition detonations were a major contributor to environmental contamination. These observations suggest that, armed with detailed information about trace signature phenomenology, new strategies and ultimately, new technologies, might be applied to maximize the tactical benefit of chemical detection.

Table 1. The number of samples collected and analyzed.

TYPE OF TRACE EXPLOSIVE RESIDUE OBSERVABLE	TYPE OF SAMPLE	
	SOILS	SURFACES
Samples Taken Co-Located with an IED-Related Threat	**19**	**43**
Background Samples Taken from Non-Live-Fire Areas	348	142
Background Samples Taken from Live-Fire "Post-Blast" Areas	215	50
Total Background Samples Taken	**563**	**192**

These results demonstrate a new framework for analyzing field chemical signature data where categorized field measurements are used to estimate signature efficacy for specific chemical sensing missions. This capability minimizes the risk and uncertainty often associated with the development of chemical sensors focused on challenging detection missions. If this new framework is to continue to be applied to challenging C-IED missions, additional field samples will need to be collected, possibly in active theaters of operation and/or in contested areas. Under these conditions, rigorous scientific collection methods must often be abandoned due to prudence associated with the circumstances. For this reason, detailed sample collection, handling, storage, and shipment studies were performed that outline acceptable "shortcuts" in field sample collection that will both maintain data quality and meet the demanding requirements of working in an active theater of operations. These results are reported in the Appendices.

2. EXPERIMENTAL METHODOLOGY

The ambitious goals of this study required that the highest quality field analysis be performed. The current EPA-approved methods for detecting explosive residues in soil are based on either high-performance liquid chromatography with ultraviolet spectrophotometric detection (HPLC-UV) as EPA Method 8330 or gas chromatography with electron capture detection (GC-ECD) as EPA Method 8095, and it is often recommended that one method be used to confirm the results from the other. In this study, specially-developed field sampling methods were used in combination with two different laboratory GC methods both based on EPA Method 8095. The sampling methods involved both surface swabbing and soil collection processes. Details of swabbing process and their use appear elsewhere {Kunz, 2008}. In addition to qualifying the sampling methods, efforts were made to establish the proper handling and storage of samples collected in the field to best enable extension of these methods to tactical environments, and a description of these procedures also appears elsewhere {Kunz, 2008}. Once the samples had been returned safely to the laboratory, they were extracted and concentrated in a method adapted from EPA Method 8330, and a description of the methods used in this study appear elsewhere as well {Kunz, 2008}. As stated above, both GC analysis methods were based on EPA Method 8095. The first used simultaneous analysis via a dual GC-ECD to reduce the need for confirmatory analysis and is called (GC-ECD)[2]. The

second method used mass spectrometric detection rather than electron capture detection. Although this sacrificed some sensitivity for the lower volatility explosive-related compounds such as RDX and TNT, it improved sensitivity for the mono- and di-nitroaromatics and obviated the need for any confirmatory analysis. Full descriptions of these methods and a detailed comparison of the two appear elsewhere {Kunz, 2008}.

3. SUMMARY OF ALL FORT IRWIN FIELD SAMPLE RESULTS

3.1. Summary of trace residues detected at Fort Irwin

The 817 field measurements made at the National Training Center at Fort Irwin, CA, on May 27-31, 2007, are summarized in Figure 1 and Tables 2 and 3, where the amounts of each of the 14 different explosive compounds measured are summed. The 14 compounds were 2,4-dinitrotoluene (2,4-DNT), trinitrotoluene (TNT), 2,6-dinitrotoluene (2,6-DNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), 4-amino-2,6-dinitrotoluene, (4Am-DNT), 2-amino-4,6-dinitrotoluene (2Am-DNT), 2-nitro-2-methylpropane-1,3-diol (NMPD), 1,3-dinitrotoluene (1,3-DNT), 3,5-dinitroaniline (3,5-DNA), pentaerythritol tetranitrate (PETN), nitrobenzene (NB), 2-nitrotoluene (2-NT), 3-nitrotoluene (3-NT), and 4-nitrotoluene (4-NT). Figure 1 shows a numerically integrated histogram of all 817 measurements made, including all backgrounds and threats, Table 2 shows the fraction of measurement in Figure 1 that were above certain mass thresholds, and Table 3 shows the aggregate sum of all trace explosive detected, broken down by compound.
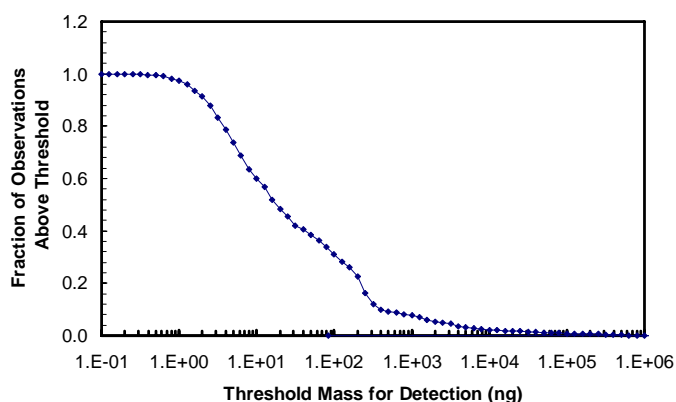

Figure 1. An integrated response histogram of all 817 samples collected at Fort Irwin.

Table 2. The fraction of observables reported in figure 1 whose values exceeded the indicated thresholds. This includes both soils (explosive mass detected per 5 gm of soil) and surfaces (explosive mass detected per 40 cm^2 of surface).

Trace Explosive Threshold Amount	Percent of Observables >Threshold
1 μg	7.7%
10 μg	2.1%
100 μg	0.86%
1 mg	0.12%
10 mg	0.0%

3

Table 3. The aggregate sum of all explosive materials measured in the 817 field samples collected at Fort Irwin, CA, from May 27-31, 2007. These results are the average of the two analysis methods. The compounds are, in descending order, 2,4-dinitrotoluene (2,4-DNT), trinitrotoluene (TNT), 2,6-dinitrotoluene (2,6-DNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), 4-amino-2,6-dinitrotoluene, (4Am-DNT), 2-amino-4,6-dinitrotoluene (2Am-DNT), 2-nitro-2-methylpropane-1,3-diol (NMPD), 1,3-dinitrotoluene (1,3-DNT), 3,5-dinitroaniline (3,5-DNA), pentaerythritol tetranitrate (PETN), nitrobenzene (NB), 2-nitrotoluene (2-NT), 3-nitrotoluene (3-NT), and 4-nitrotoluene (4-NT). Note: the NMPD was only analyzed using the GC-MS method and the total amount detected was 6.26 ng, thus the 0.12% of total designation. NA=not analyzed.

	TOTAL (ng)	% OF TOTAL
2,4-DNT	3220	61.34%
TNT	1463	27.88%
2,6-DNT	339	6.46%
RDX	185	3.52%
4AM-DNT	14.8	0.28%
2AM-DNT	14.4	0.27%
NMPD	N.A.	0.12%
1,3-DNT	3.97	0.08%
3,5-DNA	N.A.	0.03%
PETN	N.A.	0.01%
NB	N.A.	0.00%
2NT	N.A.	0.00%
3NT	N.A.	0.00%
4NT	N.A.	0.00%

4. DATA ANALYSIS METHOD

4.1 Method for analyzing the data

An observable that is not spatially correlated to any known threat and does not meet the criteria in Table 4 is called environmental clutter. Conventional wisdom states that, in a theater of operations where numerous detonations and live fire events have recently occurred, enough explosive residues exists in the form of environmental clutter that it constitutes a prohibitively high barrier to effectively localizing explosive-related threats based on their chemical signatures alone. Put another way, this conventional wisdom states that there is an abundance of trace explosive residues that do not spatially correlate with the locations of explosive threats and would thus lead to prohibitively high false alarm rates. Our analysis will attempt to both quantify this assertion and determine what constitutes a "prohibitively high" clutter level, project its quantitative impact on the ROC statistics, and suggest sensor thresholds to mitigate their effect. We recognize that these are ambitious goals and we will be careful to point out all assumptions and limitations in our analysis. Finally, it should be noted that the terms "threat" and "target" are used interchangeably as "target" refers to the fact that an explosive threat is also the "target" of a notional stand-off sensor.

In order to quantify the spatial correlation between environmental trace explosive residues and IED-related threats, the true state of both these phenomena must be obtained and is collectively referred to as the "ground truth". The "chemical" ground truth is the actual amount of signature chemicals present, and the "threat" ground truth is the actual presence or absence of an IED-related threat needing detection. Determining the spatial correlation between these phenomena will allow for prediction of the upper limit of trace detection's potential. The following sections describe methods used to determine these items.

Table 4. The attributes of an effective chemical signature.

Characteristics of an Exploitable Chemical Signature	Sensor Attribute Affected	Comments
The chemical is unique to the threat and can thus be spatially correlated to the threat	False alarm rate	Sensor independent
The signature chemical is present at concentrations sufficient to be detected	Probability of detection	Can also be used to set sensor requirements
The signature chemical persists in the environment long enough to be detected	Probability of detection	Addressed in future study
There are few, if any, interfering chemicals in the environment that might be confused for the signature chemical	False alarm rate	Sensor dependent, requires rigorous sensor testing. Beyond the scope of this study.

4.2 Determination of the "Chemical" Ground Truth

For the chemical ground truth to be meaningful in the context of this analysis, all field measurements must be made with very low minimum detectable limit (MDL) and with effectively no false alarms, and must therefore represent the actual amount of explosives present at a given measurement location. It is for these reasons that such rigorous analytical methods were employed in making these measurements. To achieve the highest possible confidence in these chemical truth observations, the average result from the $(GC-ECD)^2$ and GC-MS detection methods were used. Nevertheless, even these "gold standard" laboratory measurement methods have limitations, and thus the corresponding confidence with which it can be declared that no explosives are present at a given site is limited by the analytical method's minimum detectable limit and response variance. From the definition of method's minimum detection limit (MDL) {Kunz, 2008}, any value reported as "not detected" indicates only a 99% probability that the sample is, in fact, at zero concentration. Put another way, a zero response indicates a 1% probability that trace explosives are actually present above the MDL. Combining the results from both the $(GC-ECD)^2$ and GC-MS methods improves the detection confidence to where a zero response from both methods would indicate just a 10^{-4} probability that there are trace explosives present above their MDLs. Since no known sensor under development matches the sensitivities of these analytical methods it can be assumed that these uncertainties in "chemical truth" at low concentrations (generally <10 ng) do not impact this analysis in a significant way.

4.3 Determination of the "Threat" Ground Truth

The threat ground truth is determined more subjectively than the chemical ground truth, and is done so by personal observation of the measurement locations for all observables. Figure 2 shows representative locations of observations where the threat truth was "positive". These locations were generally created as part of troop training exercises at Fort Irwin and in all instances had elevated levels of trace explosive residue although they often did not contain bulk explosive for safety reasons. Figures 3 and 4, in contrast, show locations where the threat ground truth was "negative". In Figure 3, these were "negative" locations that had known post-blast residues and thereby represented environments one might find in an active theater of operations. In contrast, the measurement locations shown in Figure 4 were where no live-fire activity was known to have recently taken place, although we could not be 100% certain that no live-fire activities ever took place there as these measurements were all taken within active training areas of the National Training Center at Fort Irwin. We consider these environments to be representative of an unknown, hostile theater of operations where knowledge of the chemical environment was unknown.

4.4 Correlation of the Chemical and Threat Ground Truths

Given the definitions and means to categorize the chemical and threat "truths" outlined in the previous section, the next step in our analysis was to correlate the two. Figure 5 shows how correlation of the chemical and threat "truth" states can provide information regarding detection, false negatives, false alarms, and all clears. Taking all the chemical "truth" values observed when an IED threat was present (threat "truth" = TRUE) allows us to determine the fraction of IED threats

that have an associated chemical signature. This is shown schematically as the red squares in Figure 6. Likewise, we can evaluate all the chemical "truth" values for when there was no IED threat present (threat "truth" = FALSE) that have a >99.99% probability of having no trace explosives residues at greater than our methods' MDLs. This is depicted schematically as the green squares in Figure 6. Making these quantitative correlations between the Boolean states of the respective chemical and threat "truths" is the key component of the analysis described in this section, and is used to create "truth" correlations in the form of a receiver operating characteristic (ROC) curve.

Figure 2. Objects comprising "positive" threat ground truth. Clockwise from upper right, a collection of live ordnance, a in-ground cache used for hiding live ordnance, a 155-mm artillery round arranged to simulate an IED, a simulated EFP array, a single live mortar round, a buried simulated IED, an abandoned vehicle rigged with an IED, and a weapons cache in a tunnel complex.

Figure 3. Objects and/or locations comprising "negative" threat ground truth but where recent detonations had taken place. Clockwise from upper right, a fragment of a detonated 105-mm artillery round, a vehicle recently (<2 hours) used for artillery practice complete with impact craters all around it (see plastic envelopes in photo) and shrapnel scars, a VBIED rendered safe by an EOD team via C-4 detonation, a second VBIED rendered safe by an EOD team via a C-4 detonation, a fresh 105-mm impact crater, and a fresh 105-mm shrapnel fragment.

Figure 4. Objects and/or locations comprising "negative" threat truth where no known recent live-fire activity had taken place. Clockwise from upper right, military vehicle wreckage, civilian vehicle wreckage, a tire retread, a simulated VBIED event that did not use any live detonations, a suspicious roadside rock, and an abandoned vehicle muffler.

		Chemical "Truth"	
		CHEMICALS PRESENT	NO CHEMICALS
Threat Truth	**IED ACTIVITY PRESENT**	*(+) correlation* DETECTION	*No correlation* FALSE NEGATIVE
	NO THREAT PRESENT	*No correlation* FALSE ALARM	*(-) correlation* ALL CLEAR

Figure 5. Values relevant to IED detection that are obtained when combining the different Boolean outputs from the chemical and threat "truths".

		Chemical "Truth"	
		CHEMICALS PRESENT	NO CHEMICALS
Threat Truth	IED ACTIVITY PRESENT		
	NO THREAT PRESENT		

Probability that a threat has an associated signature: Detection probability driver

⊗

Probability that non-threats have associated signatures: False alarm driver

Phenomenology-based upper limit on ROC curve – the "correlation curve"
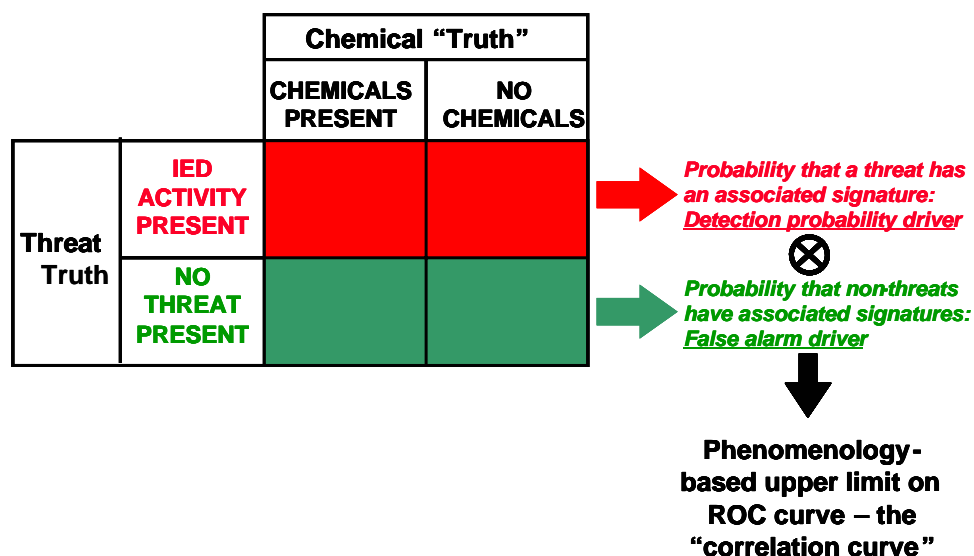
Figure 6. Method by which a phenomenology-based upper limit on a receiver operating characteristic (ROC) curve can be estimated from the statistical analysis of Boolean states of the chemical and threat "truths". See text for additional discussion.

There are some important assumptions in this analysis that must be pointed out, one of which is that all chemical measurements at a site containing an IED threat accurately represent the Boolean state of residue presence at the threat site. Put more simply, if we obtain a single chemical result near an IED, we're effectively stating that all other locations near that IED would yield the same result. This assumption is untrue, however, if the chemical residue is distributed unevenly around the IED site. For this reason, we often took several chemical measurements around a single IED site and included each of them as separate observations. For example, if a single IED site had three measurements made and only one yielded detectable amounts of explosive residue, then a correlation probability of 33% would be assigned. This is justifiable when one thinks how an actual stand-off sensor would be deployed, where an operator would scan a suspicious structure and take a finite number of measurements. The 33% number used in the above example then suggests that, based on our "chemical" truth results, the operator would have only a 33% chance of pointing his or her sensor on a surface near the IED that would register "positive", and thus only a 33% probability of detection. Although this is an acceptable way of looking at it given the data we have, the ideal approach would be to spatially map the area around each IED with a granularity that matches the spatial resolution of the notional stand-off sensor being deployed. However, this could require tens or even hundreds of measurements per site and could be prohibitively time consuming. Therefore we must live with this assumption for now.

A second assumption is that the operational backgrounds, i.e., locations where no IEDs were present, are truly representative of the types of environments where sensors will be deployed. There is, of course, no way of knowing for certain anything about some notional tactical battlespace without actually making measurements in that environment. For this study, we used the best environment available in CONUS, at the National Training Center at Fort Irwin, CA, in the heat of summer, during an active troop rotation engaging in explosive ordnance disposal and IED situational training exercise lanes, and also at the live-fire range following artillery practice from M1-A1 Abrams tanks. Short of making actual measurements in theater, this represented the best environment available to us.

4.5. Interpreting the graphs

The results of our data analysis are presented as a series of three graphs. The first is obtained by numerically integrating the aggregate results histogram and plotting the result as a function of the mass of explosive residue detected. From this, one can easily determine for a given residue amount, or mass "threshold", what fraction of those observables had measured quantities exceeding that "threshold". These plots can be made for data acquired in different operational settings (threats, backgrounds, etc.) and form the basis for all subsequent analyses. The data used to create these plots is then re-plotted where now the *x*- and *y*-axes are scaled from zero to one and represent the fraction of background and target samples, respectively, above the detection "threshold". Again, a notional data set is used to illustrate this example. The third and final type of graph relates the confidence that an observable is correlated to a threat "target" as a function of detection "threshold". Traditionally, the *detection* confidence is given by

$$\text{Confidence} = \frac{\text{Prob. of Detection}}{\text{Prob. of Detection} + \text{Prob. of False Alarm}}$$

but here we redefine it as a *correlation* confidence to mean:

$$\text{Confidence} = \frac{Fraction\ of\ Observations\ That\ Correlate\ to\ Threats}{Total\ Fraction\ of\ Observations}$$

5. AGGREGATE ANALYSIS OF ALL EXPLOSIVE MATERIALS DETECTED

The observables from Fort Irwin can be separated into two threat categories, "threat" and "background", where the "threat" category refers to an observable that is spatially coincident with an IED-related threat. Examples of "threats" were described in Section 4.2.2. The "background" observables are further divided into two sub-categories, those from live-fire areas and those from areas where no live-fire activities recently took place. Finally, there are two types of samples, soils and surfaces. Table 1 listed all the categories of observables, their notations used in subsequent graphs, and the numbers of each sample type used in the analysis.

Figures 7-9 provide a top-level summary that includes all 755 background samples and all 62 IED-threat related samples. Figure 7 shows that the correlation of environmental explosive residue in a theater of operations to known IED threats is weak, with the best correlation occurring for trace levels equal to or greater than 1,000 ng (1 μg), where 27% of all threats had residue levels exceeding 1 μg whereas only 6.6% of the background locations measured at Fort Irwin have residue levels exceeding 1 μg, yielding a correlation confidence of ~81% for this threshold level. From a sensing perspective, this level of spatial correlation is not amenable to low false-alarm-rate tactical sensing. For this reason, this same analysis was repeated on various subsets of the data to identify the best sample types, CONOPs, and signature chemicals, and thus the conditions where the best sensor performance would be expected. Figures 10-12 and Figures 13-15 split the previous results out by soil and surface samples, respectively, where the soil samples are in units of nanograms of explosive per 5 grams of soil and the surface results in units of nanograms of explosive per ~40 cm^2 of surface area. In these figures, we have also broken out the operational background (recent live fire versus no recent live fire). Here, we see significant differences between these two background operating environments for both soil and surface sample types, suggesting that the presence of artillery and EOD detonations contribute to the background in measureable ways and reduce the spatial correlation between trace explosive residues and explosive threats. For example, for both soils and surfaces, the correlation confidence was >95% and the fraction of threats with residue amounts exceeding 1 μg >40% in the normal background. However, the correlation confidence drops to between 70 and 85% for the live-fire background (Figures 12 and 15).
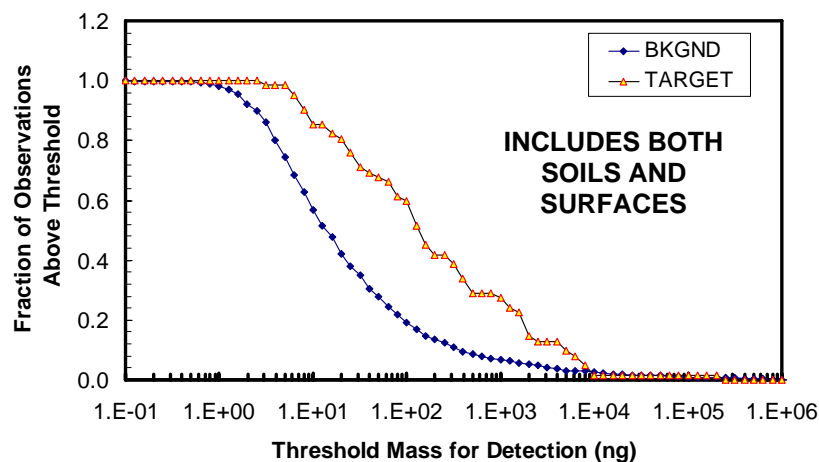

Figure 7. A summary of all threat, or "target" observables and all non-threat, or "background" observables as a function of the mass detected of all the explosives analyzed. See Section 4.2.2 for our definition of a "threat". These data include both soil (ng per 5 grams of soil) and surface swabs (ng per ~40 cm^2 of surface) and include background data from both Fort Irwin's live fire areas and non-live-fire areas.
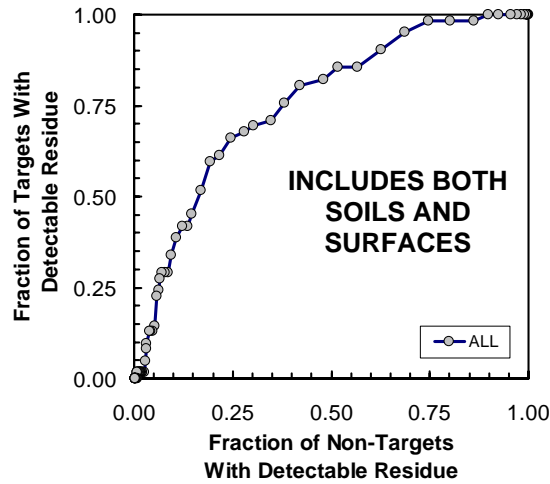
9

Figure 8. Comparison of the fraction of IED threats ("targets") to non-target backgrounds that have detectable amounts of residue for all samples collected at Fort Irwin. See Section 4.2.2 for our definition of a "threat". These data include both soil and surface swabs, and include background data from both Fort Irwin's live fire areas and non-live-fire areas.
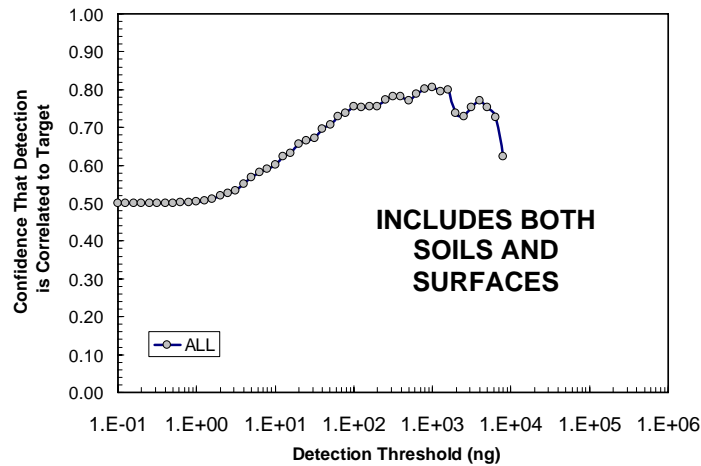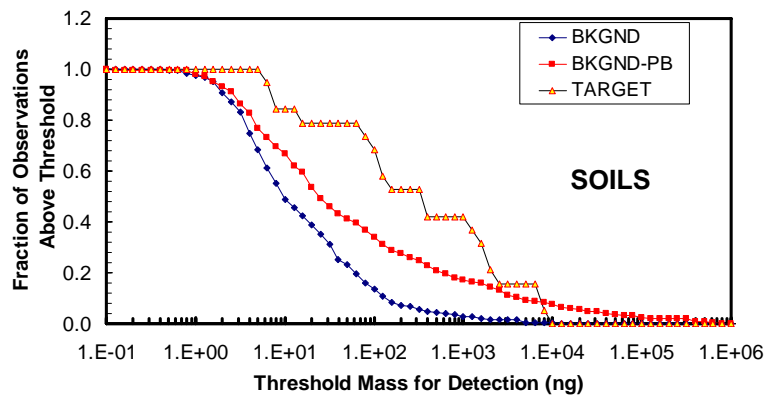

Figure 9. The confidence that any observation of explosives from Fort Irwin was spatially correlated to a "threat". See Section 4.2.2 for our definition of a "threat". This data set included both soil and surface swabs, and includes background data from both Fort Irwin's live fire areas and non-live-fire areas.

Figure 10. A summary of all threat, or "target" observables and all non-threat, or "background" observables measured in soils (ng per 5 grams of soil) as a function of the mass detected of all the explosives analyzed. See Section 4.2.2 for our definition of a "threat". Here, the background "non-threat" samples were plotted separately as being either from live-fire, post-blast areas (BKGND-PB) or from areas where no known live-fire activities recently had been conducted (BKGND).
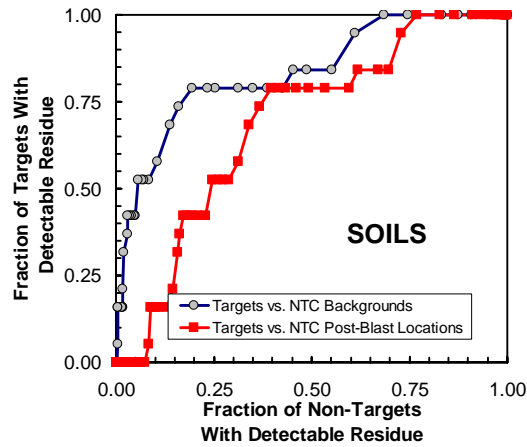
10

Figure 11. Comparison of the fraction of IED threats ("targets") to non-target backgrounds that have detectable amounts of residue for soil samples collected at Fort Irwin. See Section 4.2.2 for our definition of a "threat". Here, the background "non-threat" samples were plotted separately as being either from live-fire, post-blast areas or from areas where no known live-fire activities recently had been conducted.
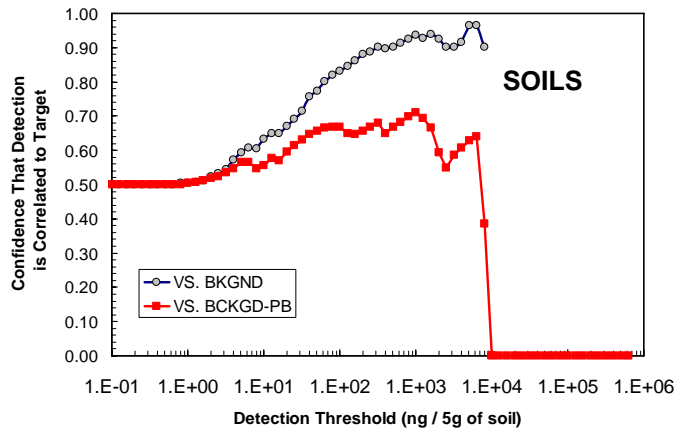

Figure 12. The confidence that any observation of explosive residues in soils from Fort Irwin was spatially correlated to a "threat". See Section 4.2.2 for our definition of a "threat". Here, the background "non-threat" samples were plotted separately as being either from live-fire, post-blast areas (BKGND-PB) or from areas where no known live-fire activities recently had been conducted (BKGND).
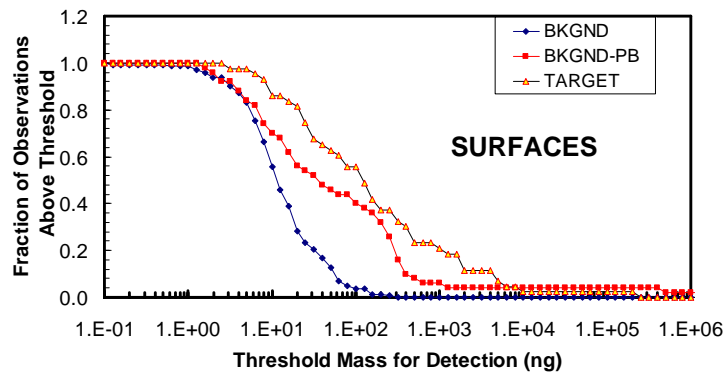

Figure 13. A summary of all threat, or "target" observables and all non-threat, or "background" observables measured on surfaces (ng per 40 cm² of surface) as a function of the mass detected of all the explosives analyzed. See Section 4.2.2 for our definition of a "threat". Here, the background "non-threat" samples were plotted separately as being either from live-fire, post-blast areas (BKGND-PB) or from areas where no known live-fire activities recently had been conducted (BKGND).
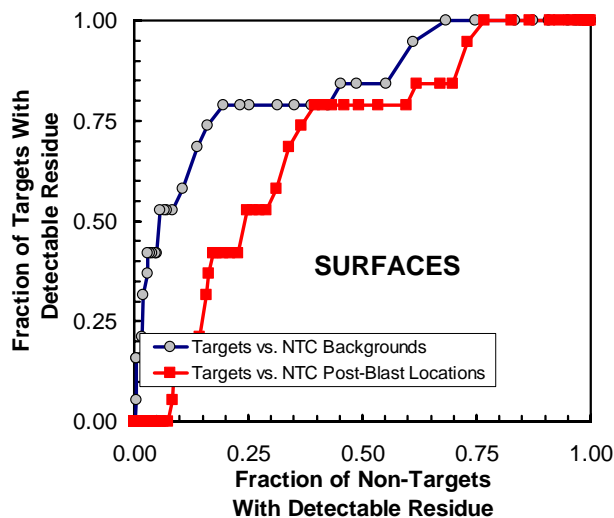
11

Figure 14. Comparison of the fraction of IED threats ("targets") to non-target backgrounds that have detectable amounts of residue for all surface samples collected at Fort Irwin. See Section 4.2.2 for our definition of a "threat". Here, the background "non-threat" samples were plotted separately as being either from live-fire, post-blast areas or from areas where no known live-fire activities recently had been conducted.
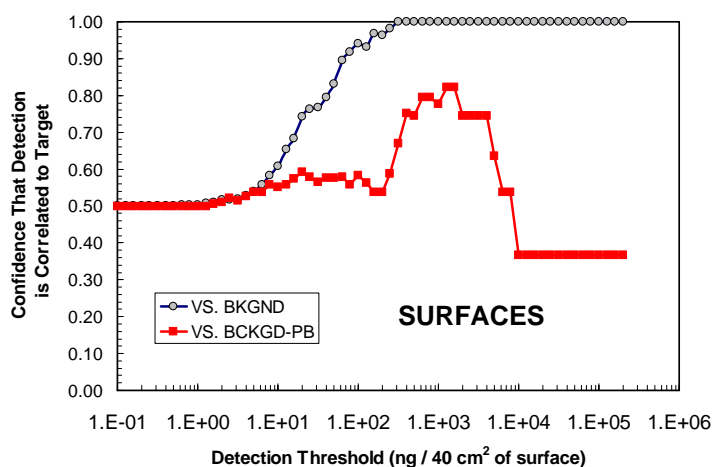

Figure 15. The confidence that any observation of explosive residues on surfaces from Fort Irwin was spatially correlated to a "threat". See Section 4.2.2 for our definition of a "threat". Here, the background "non-threat" samples were plotted separately as being either from live-fire, post-blast areas (BKGND-PB) or from areas where no known live-fire activities recently had been conducted (BKGND).

6. SUMMARY AND CONCLUSIONS

6.1 Analysis summary

Figures 16 and 17 provide a comparison of three of the more common chemicals detected, RDX, TNT, and 2,4-DNT. From these figures, we see that RDX is the better signature compound of the three. Also, Tables 5 and 6 summarize some key numbers extracted from the numerous graphs presented earlier in this section. The most important finding is that trace explosive residues in the environment, even for the live-fire areas at Fort Irwin are, for the most part, spatially correlated to the presence of IED-related threats. However, this correlation is weak and weakens further when the background contains post-blast residues.
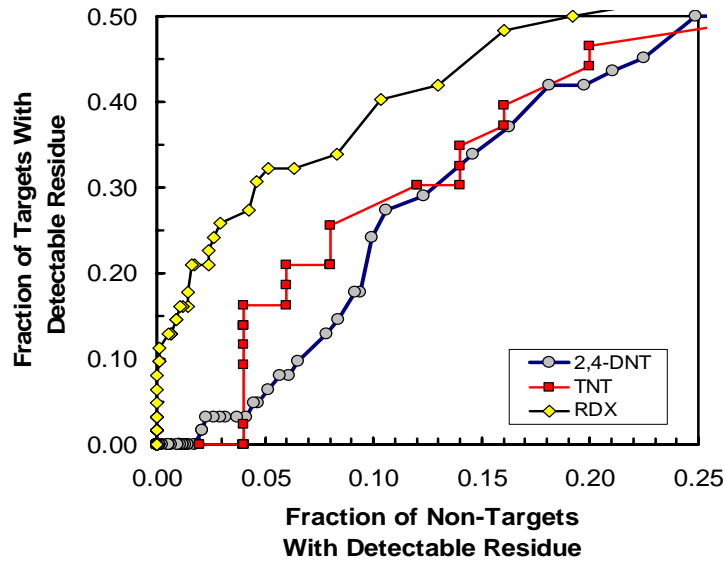
12

Figure 16. Comparison of the correlation of RDX, TNT, and 2,4-DNT between threats ("targets") and non-threats ("non-targets") for all sample types and operating environments. The sample types include both soils and surfaces and the operating environments include areas both with and without recent live-fire activities. From this data, it can be concluded that environmental RDX is best correlated to the presence of threats, and is therefore the best indicator of threats at Fort Irwin.
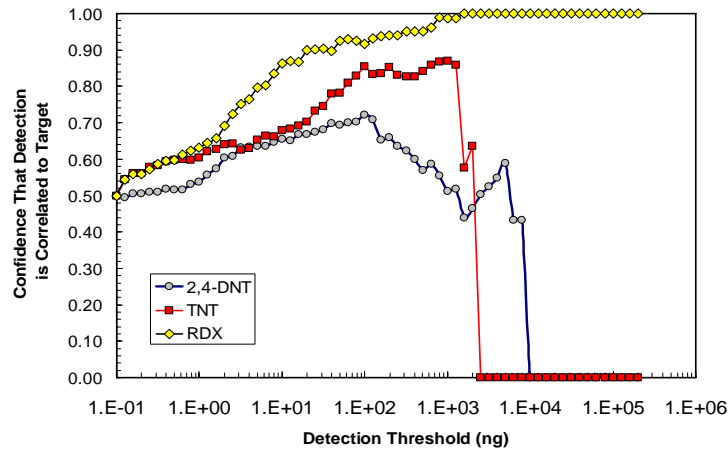

Figure 17. Comparison of the signature-target correlation confidence for RDX, TNT, and 2,4-DNT. From this, we see that RDX is most often spatially correlated to an IED-related threat with >90% of all RDX observations for thresholds between 100 ng and 1 mg being associated with an IED threat. 2,4-DNT shows the poorest correlation, driven largely by the prevalence of background 2,4-DNT caused by artillery round detonations.

Table 5. Data analysis summary. These values were extracted from the plots presented in section 4.3. Here, PFA is defined as the fraction of background observations whose levels exceeded the stated threshold (thr (ng)) and PD is defined as the fraction of threats that have an associated trace explosive signature above the stated threshold. Thus, the PD value represents an upper limit on the actual detection probability for any real sensor whose MDL is equivalent to the combined (GC-ECD)[2] and GC-MS methods (~1-10 ng).

PFA	Sample Type	Background Type	TNT			RDX			2,4-DNT			Am-DNT			All Compounds		
			PD	Conf	Thr (ng)	PD	Conf	Thr (ng)	PD	Conf	Thr (ng)	PD	Conf	Thr (ng)	PD	Conf	Thr (ng)
1%	Soils	No Live Fire	0.16	0.93	160	0.25	0.95	20	0.11	0.90	3200	0.32	0.97	160	0.16	0.92	4200
		Live Fire	0.00	0.00	20000	0.00	0.00	550	0.00	0.00	350000	0.05	0.79	2000	0.00	0.00	320000
	Surfaces	No Live Fire	0.21	0.94	70	0.22	0.95	70	0.25	0.96	45	0.02	0.62	65	0.37	0.96	220
		Live Fire	0.00	0.00	630000	0.19	0.94	280	0.00	0.00	2300000	0.00	0.00	6500	0.00	0.00	>2000000
		All	0.02	0.58	1600	0.15	0.94	170	0.00	0.00	50000	0.08	0.88	400	0.02	0.37	100000
PFA	Sample Type	Background Type	TNT			RDX			2,4-DNT			Am-DNT			All Compounds		
			PD	Conf	Thr (ng)	PD	Conf	Thr (ng)	PD	Conf	Thr (ng)	PD	Conf	Thr (ng)	PD	Conf	Thr (ng)
5%	Soils	No Live Fire	0.32	0.83	35	0.32	0.86	7	0.26	0.84	150	0.37	0.88	16	0.42	0.90	380
		Live Fire	0.05	0.51	500	0.20	0.80	27	0.00	0.00	11000	0.31	0.85	180	0.00	0.00	22000
	Surfaces	No Live Fire	0.33	0.87	170	0.33	0.86	7	0.39	0.88	16	0.09	0.65	25	0.56	0.92	80
		Live Fire	0.16	0.77	1400	0.19	0.92	110	0.03	0.57	700	0.03	0.32	110	0.19	0.80	1100
		All	0.24	0.84	80	0.32	0.86	10	0.50	0.50	1000	0.12	0.70	35	0.13	0.73	2100
PFA	Sample Type	Background Type	TNT			RDX			2,4-DNT			Am-DNT			All Compounds		
			PD	Conf	Thr (ng)	PD	Conf	Thr (ng)	PD	Conf	Thr (ng)	PD	Conf	Thr (ng)	PD	Conf	Thr (ng)
10%	Soils	No Live Fire	0.37	0.76	18	0.43	0.81	4	0.65	0.80	70	0.37	0.64	8	0.58	0.85	125
		Live Fire	0.32	0.74	80	0.32	0.76	9	0.11	0.51	2000	0.32	0.76	40	0.16	0.61	4000
	Surfaces	No Live Fire	0.40	0.80	8	0.42	0.82	4	0.40	0.77	7	0.13	0.58	17	0.61	0.90	65
		Live Fire	0.27	0.74	35	0.49	0.83	3	0.23	0.70	63	0.13	0.58	17	0.30	0.75	400
		All	0.31	0.75	32	0.40	0.80	5	0.27	0.72	100	0.23	0.69	16	0.38	0.78	330

Table 6. A breakdown of signature correlation at a fixed detection threshold of 1 μg. Here, PFA is defined as the fraction of background whose levels exceeded the 1 μg threshold, and PD is defined as the fraction of threats that have an associated trace explosive signature whose level exceeds the 1 μg threshold. Thus, the PD value represents an upper limit on the actual detection probability for any real sensor whose MDL is equivalent to the combined (GC-ECD)[2] and GC-MS methods (~1-10 ng).

Sample Type	Detection Threshold	Max PD	Min PFA	Confidence
Targets in soils at Fort Irwin	1 μg / 5 g soil	42%	3%	0.94
Targets in soils at Fort Irwin's live fire areas	1 μg / 5 g soil	42%	17%	0.77
Surface residues at Fort Irwin	1 μg / 40 cm²	21%	<1%	>0.995
Surface residues at Fort Irwin live fire areas	1 μg / 40 cm²	21%	6%	0.78
All samples in all areas from Fort Irwin	1 μg	27%	7%	0.81
Other detection thresholds:				
Surface residues at Fort Irwin	160 ng / 40 cm²	42%	1%	0.97
Surface residues at Fort Irwin live fire areas	1.3 μg / 40 cm²	19%	4%	0.82

5.2 Conclusions

Combining background data with estimated target analyte signature data has allowed us to perform statistical analyses of well populated signature/background data sets. When combined with explosives signatures, an estimation of both PD and PFA for different contingency operations, sensing targets, and sensing modalities can be made. This analysis assumes a sensor that matches the combined sensitivity and selectivity of the GC-MS and (GC-ECD)[2] methods used in collecting the data. However, it is unlikely that actual field sensors will be able to match this performance and thus our estimates represent a "best case" detection capability. Even for the best case detection scenario, our analysis estimates that tactical use of explosives detection to locate IEDs and/or IED-related threats will likely not support high detection

probabilities (i.e., <50% PD at best) or low false alarm rates (i.e., >5% PFA likely) This is because, although explosive residues <u>are</u> spatially correlated with IED-related threats, the correlation is weak. Specifically, it was determined that 27% of all IED-related threats exhibited trace explosive residues exceeding 1 μg on/in their immediate vicinity, whereas for general background measurements this fraction was <1%. However, 6% of background measurements taken from live-fire areas recorded contamination levels in excess of 1 μg. A greater understanding of explosives residue fate and transport is needed to further refine these estimates.

5.3. Implications for tactical sensing

Although the initial conclusions summarized in the previous section may seem discouraging, the data in this report also suggests that new strategies may be possible that might provide capabilities not afforded by currently pursued detection strategies. Such strategies might involve development of sensors that detect only specific compounds, or that are only deployed for specific sample locations. For example, it was determined that RDX residues on surfaces, detected at low threshold (<300 ng) might afford modest detection probabilities of ~20% but maintain false alarm rates <1%. Likewise, it was determined that 2,4-dinitrotoluene residue in soils caused by munition detonations were a major contributor to environmental contamination. Thus, we can conclude that the simple ability to discriminate between RDX and 2,4-dinitrotoluene, and to employ contextual discrimination between surfaces and soils, might enable a modest capability even in highly contaminated environments. When combined with other sensor inputs or intelligence, such a modest capability might provide tactically useful information.

From the graphs and tables presented in this report, we can make the following more detailed conclusions about what was learned at Fort Irwin:

For a sensor that does not discriminate between different organonitrate explosives:

- The probability of detection will likely be no higher than 30% to 60%, depending on the detection threshold. This stems from the nature of trace explosive signatures, where some threats may simply not have accessible signatures due to handling, weathering, shadowing from the sensor, etc.
- The confidence that a trace explosive observable is spatially correlated to an IED-related threat and is thereby useful in identifying that threat decreases from the 85-95% range down to the 70-85% range when the background theater of operations is contaminated with recent post-blast residue.
- The optimal detection threshold, when considering both the probability of detection and the alarm confidence, should be <1 μg. Sensors incapable of detecting amounts this small will have a low probability of detection (<30%). This is because most IED-related threats simply don't have that much trace explosive residue available for sensing.

Assuming the ability to discriminate different organonitrate explosives exists:

- The best signature is RDX on surfaces. Here, we define "best" as meaning the highest probability of detection and the highest confidence. Our observations showed that few, if any, post-blast background contamination resulted in RDX surface contamination.
- The biggest source of background clutter was 2,4-DNT located in soils that resulted from artillery round detonations.
- Only a small subset of organonitrates is present in sufficient abundance around IED threats to be considered as useful signature compounds. Those include TNT, RDX, 2,4-DNT, 2,6-DNT, 2-Am-4,6-DNT, and 4-Am-2,6-DNT. All other compounds, including TNB, 1,3-DNT, DNB, 3,5-DNA, NB, 2-NT, 3-NT, and 4-NT, were not useful as a signature capable of supporting a high probability of detection.

Furthermore, ECBC found in separate measurements, reported in Analytical Test Report 0238-101507, that minimal energetic or energetic related residues are present in the headspace of explosive devices. Comparison of blank control, sorbent tube and bag extract also found no major chemical signature differences in the off-gassing compounds useful for round identification. These observations suggest that, armed with detailed information about trace signature phenomenology, new strategies and ultimately, new technologies, must be applied to maximize the tactical benefit of chemical detection.

6. ACKNOWLEDGMENTS

7. REFERENCES

SW-846 Method 8095: Explosives by Gas Chromatography, Revision 0, Available from http://www.epa.gov/SW-846/pdfs/8095.pdf. Accessed February 2007.

"Method 8330: Nitroaromatics and nitramines by High Performance Liquid Chromatography (HPLC)."

Kunz, R. R., Clow, K. E.; Hardy, D.; Switkes, M.; Krohn, K. E.; Ostazeski, S. A.; Oyler, J. M., Fountain, A. W. III; Final Report: Quantitative Analysis of Trace Explosive Residues found at the National Training Center in Fort Irwin, CA, U.S. Army Edgewood Chemical and Biological Center, May, 2008 (in preparation).

Ostazeski, S. A.; Oyler, J. M., Fountain, A. W. III, Edgewood Biological and Chemical Center, Analytical Test Report 0238-101507, 2007.